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A METHOD FOR MANUFACTURING A POLYETHER HALOHYDRIN
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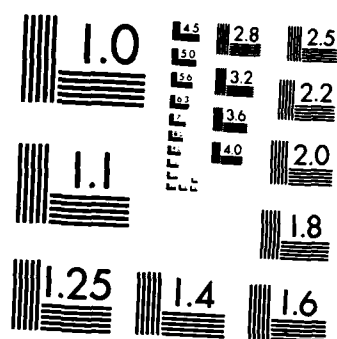
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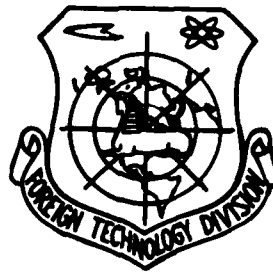
FOREIGN TECHNOLOGY DIVISION



A METHOD FOR MANUFACTURING A POLYETHER HALOXYDRIN
POLYMER AND ITS DERIVATIVES

by

Tsutomu Toi and Domitsu Sakamoto



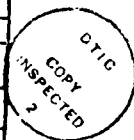
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By: Tsutomu Toi and Domitsu Sakamoto

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(54) A METHOD FOR MANUFACTURING A POLYETHER
HALOHYDRIN POLYMER AND ITS
DERIVATIVES

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Specifications

Detailed Explanation of Invention

This invention pertains to a method for manufacturing a polyether halohydrin polymer, which is obtained by addition polymerization of epihalohydrin with alcohol molecules, and its derivatives.

The aforementioned polymer is a new substance. It is used as an intermediate for polyester urethane resins and surfactants and as an improving agent and intermediate for cellulose. Its derivatives are used as starting materials, improving agents, and reactivity solvents for epoxy resins, paints and glues, improving agents and reinforcing agents for synthetic resins and fibers, and as stabilizers for chlorine-containing resins. Many other applications are also anticipated.

Heretofore, the method whereby epichlorohydrin is polymerized in the presence of a catalyst, such as sulfuric acid, phosphoric acid, tin tetrachloride, titanium tetrachloride and boron trifluoride, has been well known. However, an efficient method for addition polymerization of epihalohydrin with alcohol molecules was not known.

This invention pertains to a method for manufacturing a polyether halohydrin polymer which is characterized by the fact that epihalohydrin is addition polymerized with alcohol molecules in the presence of perchloric acid or periodic acid as the catalyst.

Furthermore, this invention also pertains to a method for manufacturing a polyether polyepoxy polymer, which is obtained by treating the aforementioned polyether halohydrin polymer with an

alakline substance.

Monohydric alcohols, such as methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, octyl alcohol, dodecyl alcohol, and octadecyl alcohol, dihydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, isobutylene glycol, 1,6-hexane diol, etc., trihydric alcohols, such as glycerine, glycerol, monochlorhydrin, trimethylol propane, trimethylol ethane, triethanol amine, etc., and polyhydric alcohols, such as pentaerythritol, sorbitol, hexahydrohydroquinone, etc. can be mentioned as the alcohols used as reaction substrates in this invention that have a hydroxyl radical in their molecules. These alcohols have a starting and accelerating effect on epihalohydrin in the addition polymerization reaction.

Epichlorhydrin, epibromhydrin, and methylepichlorhydrin can be used for the epihalohydrin that is to be addition polymerized with alcohol molecules. Moreover, other compounds having an epoxy radical in their molecules, such as ethylene oxides propylene oxides or mixtures of these, may also be used in addition polymerization.

Perchloric acid or periodic acid can be used as the catalyst in this invention. Perchloric acid is particularly preferred.

The method in this invention can be executed by addition polymerization of epihalohydrin after the catalyst and epihalohydrin have been added to alcohol with or without a solvent and heated for a specified amount of time. After polymerization, the catalyst is removed and the polymer is rinsed with water. When a solvent or a substance with a low volatility is present, these should be removed by distillation under reduced pressure to obtain

a polyether halohydrin polymer. Furthermore, a polyether polyepoxy polymer can be easily manufactured by alkali treatment of the polyether halohydrin polymer. In this case the method whereby /212 epoxidation is directly carried out without extracting the catalyst after the aforementioned polymer reaction is efficient from an industrial viewpoint.

The polymerization reaction is completed within a relatively short amount of time. The polymerization temperature is 150°C or less, and preferably, $20-100^{\circ}\text{C}$. Although the method in this invention may be carried out with or without a solvent, when necessary it should be carried out in the presence of halogenous hydrocarbons, such as methylene chloride, ethylene dichloride, chloroform, methyl chloroform, and carbon tetrachloride, ethers, such as diethyl ether, diisopropyl ether, etc., aliphatic hydrocarbons, aromatic hydrocarbons, etc. The catalyst can be removed by rinsing the product with the equivalent of an alkaline solution after polymerization.

It is preferred that 0.05-5 molar% of catalyst per 1 mole of epihalohydrin and 0.01-10 moles of alcohol per 1 mole of epihalohydrin be used in this method.

When a dihydric alcohol is employed as the reaction substrate in this invention, a polyether halohydrin polymer having 2 individual halohydrins among its molecules is obtained. In the case of a polyhydric alcohol, a polyether halohydrin polymer having about the same number of hydroxyl radicals is obtained. Moreover, the degree of polymerization of the polyether halohydrin polymer depends on the molar ratio of alcohol and epihalohydrin. Although any degree of polymerization is possible the degree of polymerization can be increased with an

increase in the molar percentage of the epihalohydrin. The polymer obtained in this way is a liquid that easily becomes thick in most organic solvents, other than water and aliphatic hydrocarbons.

A derivative of the polyether halohydrin can be obtained by treating the polyether halohydrin in this invention with an alkali with or without a solvent. It is preferred that alkaline metallic compounds, such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, or potassium bicarbonate, be used as the alkali in this invention. However, calcium hydroxide, barium hydroxide, magnesium hydroxide, iron hydroxide, aluminum hydroxide, or oxides of these metals may also be used. The polyether epoxy polymer obtained in this way is a liquid that easily becomes thick in most organic solvents and can be cured with conventional epoxy resin curing agents.

Each of the polymers obtained with the new method from this invention have superior properties. Moreover, they can be used as industrial intermediates or as industrial starting materials and chemicals by themselves or in mixtures with other substances. Further expansion of their application range is anticipated.

Example 1

78.7 g of ethylene glycol was placed in a reaction container. 85 g of 10% perchloric acid was added by drops while the mixture was stirred at room temperature. Then 555 g of epichlorhydrin was added by drops for about 15 hours while the mixture was kept at a temperature of about 70°C. When this process was completed, polymerization was carried out for 5 hours at a temperature of 70-75°C to obtain a thick liquid. This part was removed and

the volatile components were distilled off for 1 hour at 5 mm Hg and 70 °C. 99.5% was residue. The residue catalyst in the polymer was rinsed with 300 ml of water containing an equivalent amount of ammonia until the rinsing solution became neutral. Then it was dried under reduced pressure at 70 °C. The polymer that was obtained was a thick liquid with a viscosity of 21 PS (25 °C). When the degree of polymerization was measured with the vapor pressure depression method, the number of moles of epichlorhydrin added to ethylene glycol was 45.

Example 2

While the temperature of a mixture of 461 g of ethyl alcohol and 370 g of epichlorhydrin was kept at about 70 °C, 114 g of 80% periodic acid was added by drops for 15 hours while the mixture was stirred. Polymerization was then carried out for 7 hours at a temperature of 65-70 °C. The residue catalyst was neutralized with sodium bicarbonate and rinsed with water. When the product was dried under reduced pressure at 60 °C, a thick liquid with a viscosity of 15 PS (25 °C) was obtained at a yield of 98.2%.

Example 3

While the temperature of a mixture of 13.4 g of trimethylol propane and 92.5 g of epichlorhydrin was kept at about 80 °C, 28.8 g of 70% perchloric acid was added by drops for 2.5 hours. Then the reaction was continued for another 5 hours at a temperature of 80-95 °C. The operation after the reaction was exactly the same as in Example 2. A thick liquid with a viscosity of 38 PS (25 °C) was obtained at a yield of 98.6%.

Example 4

While a mixture of 92.1 g of glycerine and 111.0 g of epichlorhydrin was kept at a temperature of 45-50° C, 28.8 g of 70% perchloric acid was added by drops for 3.5 hours. The reaction was continued for another 4 hours at 65-70° C. The same treatment as in Example 2 was carried out. A thick liquid with a viscosity of 830 PS (25° C) was obtained.

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Example 5

While a mixture of 11.8 g of 1,6-hexamethylene diol, 7.2 g of 70% perchloric acid, and 100 ml of ethylene dichloride was being stirred, 41.6 g of epichlorhydrin was added by drops for 3 hours at 65-70° C. Then the reaction was continued for 4 more hours at the same temperature. After the mixture had cooled, it was rinsed with 200 ml of water containing an equivalent amount of sodium bicarbonate and 100 ml of water. After the solvent was distilled off, the mixture was dried under reduced pressure at 70° C. A thick liquid with a viscosity of 25 PS (25° C) was obtained at a yield of 98.5%.

Example 6

While a mixture of 13.6 g of pentaerythritol, 28.8 g of 70% perchloric acid, and 20.0 g of methyl chloroform was being stirred, 138.0 g of epichlorohydrin was added by drops for 3 hours at a temperature of 60-70° C. The reaction was continued for 5 more hours at 60-65° C. After the mixture was cooled and the same treatment as in Example 5 was carried out, a thick liquid with a viscosity of 72 PS (25° C) was obtained at a yield of 98.7%.

Example 7

62.0 g of the polymer obtained in Example 1 was dissolved

in 120.0 g of toluene. Then 13.0 g of sodium hydroxide was added over a period of 1 hour at a temperature of 40 °C or less. Then the reaction was continued for 1 more hour at the same temperature. The reaction product was rinsed until it was neutral. The solvent was distilled off and when the product was dried, 50.7 g of residue liquid was obtained. When the infrared absorption spectrum was studied, strong absorption at 3200-3600 cm^{-1} was seen prior to alkali treatment. However, this absorption was not observed after treatment. The liquid had a viscosity of 131 (25 °C) and displayed 7.4% oxylane oxygen.

Example 8

42.0 g of the polymer obtained in Example 2 was dissolved in 100.0 g of benzene. Then 6.6 g of sodium carbonate was added over a period of 1 hour at a temperature of 40 °C or less. The reaction was continued for two more hours. After the mixture was cooled, it was rinsed and concentrated. A liquid with a viscosity of 110 cps (25 °C) and oxylane oxygen content of 4.1% was obtained.

Example 9

21.0 g of the polymer obtained in Example 3 was dissolved in 60.0 g of benzene. Then 6.0 g of sodium hydroxide was added over a period of 1 hour at a temperature of 40 °C or less. The reaction continued for 2 more hours. After being cooled to room temperature, the product was rinsed until it was neutral and the solvent was distilled off under reduced pressure. 18.5 g of a thick liquid with a viscosity of 650 cps (25 °C) and oxylane oxygen content of 4.6% was obtained.

(57) Scope of Patent Claim

1. A method for manufacturing a polyether halohydrin polymer which is characterized by the fact that epihalohydrin is addition polymerized with alcohol molecules in the presence of a perchloric acid or periodic acid catalyst.

(56) References

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